January 25, 1968

Office of Research Grants and Contracts
Code BG
National Aeronautics and Space Administration
Washington, D. C.   20546

Subject: IITRI G6003-Q6
           "Metal Carbide-Graphite Composites"
           Contract No. NASr-65(09)

Gentlemen:

I.   INTRODUCTION

Metal carbides are the most refractory of all known
materials and also exhibit high strength. Their use for high
temperature applications has been limited by their suscepti-
bility to thermal shock and also by difficulties in the machin-
ing of desired configurations. However, the incorporation of
graphite to form a series of metal carbide-graphite composites
has yielded dense, well-bonded materials which minimize the
undesirable properties of pure carbides while exploiting their
high strength.

Our earlier work[1] has dealt with the fabrication and
characterization of a wide variety of metal carbide-graphite
composites with particular emphasis on the NbC-C and TaC-C
systems. The materials were hot-pressed at temperatures of
2600° to 3250°C using no binder. Solid and/or liquid state
sintering under pressure at these high temperatures is the mech-
anism by which the raw powder mixture is consolidated into a

a dense two-phase body. An extensive study has been conducted of various compo   -tions and their properties at both room temperature and temperatures up to 2800°C. These data have provided a broad picture of behavior in the various systems and the property trends which may be expected as a function of carbide content in any particular system. In general, the NbC-C and TaC-C systems were found to exhibit superior structural integrity at high temperatures.

The purpose of this year's work is to build on the broad base of information which has been established and to obtain a better insight into control of properties. The studies to date have shown how this may be done by raw material choice, e.g., incorporating carbons which have different processing histories, particle morphology, and purity levels. Less anisotropy and greater creep resistance are two of the properties being developed for the NbC-C composites. The specific studies which are being conducted are as follows:

1. Carbon Source - Variations in carbon source which contrast with the needle coke used in earlier studies are being evaluated.

2. Particle Size and Shape - These parameters are being varied so as to obtain different size relationships between the graphite and carbide phases, in an attempt to control composite properties.

3. Use of Sintering Aids - Small amounts of additives will be incorporated in the TaC-C system to obtain liquification at temperatures lower than the 3450°C eutectic temperature. This will permit exploitation of the densification and improved bonding obtainable in liquid phase sintering at processing temperatures of 3200°C or lower.

4. Properties Evaluation - The effects of the above men-
tioned variables upon physical and mechanical properties of
composites in both grain directions are being determined. Parti-
cular attention is being paid to creep behavior of these mate-
rials at temperatures of 2500°C and higher. Attempts will be
made to develop properties conducive to good thermal shock
resistance, i.e., increased strength and thermal conductivity,
and decreased elastic modulus and coefficient of expansion.

During this period, study of the effects of using dif-
ferent carbon sources for NbC-C composites has been continued.
High temperature flexural strength, flexural creep, and thermal
expansion up to 2550°C have been determined for the various
materials.

II. DISCUSSION

In previous work[1] the source for the graphite phase
in our metal carbide-graphite composites has been calcined pet-
roleum coke (CPC). This material consists of needle-like parti-
cles which are of 3.1μ particle size. The studies which are
presently being conducted involve incorporation into NbC-C com-
posites of other carbon powders of differing morphology and
processing histories in an attempt to control properties such
as strength, degree of anisotropy and high temperature behavior.
The powders which have been evaluated include graphites, cokes
and carbon blacks. Two of the carbons were obtained from the
CMB-6 Section of LASL. Both M-2 graphite flour and Varcum have
received considerable study by CMB-6, and have been included
for comparative tests. Other carbons such as Gilsonite coke
and Thermax were chosen to obtain more isotropic properties,
since their particles can be considered "spherical" as opposed
to the needle coke (CPC) or platy Ceylon graphite which have
been shown to increase anisotropic behavior.

In addition NbC powders of different morphology have also been evaluated. Although room temperature data were quite similar for the various composites, high temperature measurements reveal significant differences in behavior. The results are described in the following sections.

A.   Raw Materials

1.   Carbon Sources

Eight carbons have been considered in this study. Six of these which have been described more fully in the last report[2] are:

1.   Varcum (V) - A glassy resin coke prepared by the CMB-6 Section[3] at Los Alamos Scientific Laboratory (LASL). Particle size range - 44 to 100μ.

2.   M-2 (M2) - A graphite flour, also from CMB-6:LASL.[3] Particle size range - 44 to 100μ.

3.   Calcined petroleum coke (CPC) - A needle coke with average particle size of 3.1μ.

4.   Ceylon graphite (Cy) - A fine natural graphite, 1 to 5μ.

5.   Gilsonite (G) - A somewhat harder coke than CPC. Used in a particle size of less than 74μ.

6.   Thermax (Th) - A fine carbon black with average particle size of about 0.4μ.

Two additional carbons have also been incorporated into NbC-C composites for evaluation. These are:

1.   Sterling 10R (S10R) - A very fine carbon black with particle diameter of less than 0.1μ. Obtained from Cabot Corporation.

2. High expansion graphite (Hex) - A <u>high thermal expansion isotropic graphite</u> powder of less than 44μ. This material was milled from rod stock by Union Carbide at Lawrenceburg, Tennessee.

The Sterling 10R carbon black was chosen for study since it closely resembles lampblack. Lampblack-base graphite has been reported to exhibit much less creep than a coke-base graphite such as ATJ (Union Carbide) under the same stress-temperature conditions.[4] The high expansion graphite is a development of Union Carbide and is produced from a high thermal expansion isotropic airblown coke.

Metallographic examination of these powders appear in Fig. 1. The high expansion graphite (Hex) is similar in appearance to M-2 graphite, and is not needle-like or platy as are CPC or Ceylon graphite. The extremely fine particle size of S10R is evident from the 1000 magnification photomicrograph.

2. <u>NbC Powders</u>

A very fine NbC powder was supplied by N-1:LASL for evaluation. This material, which will be referred to as Blend Nb-2, has an average particle size of 0.157μ as calculated from surface area (BET) measurements. As seen in the metallographic photographs in Fig. 2, Blend Nb-2 is much finer than the Wah Chang (SP26713C) material. Under higher magnification (1000X, Fig. 2c) the powder appears to be aggregates of the fines, corresponding to "Type C" as defined by Riley.[5]

NbC-30B obtained from LASL is quite similar in particle size and shape to the Wah Chang NbC. Photomicrograph of the former was included in the most recent report.[2]
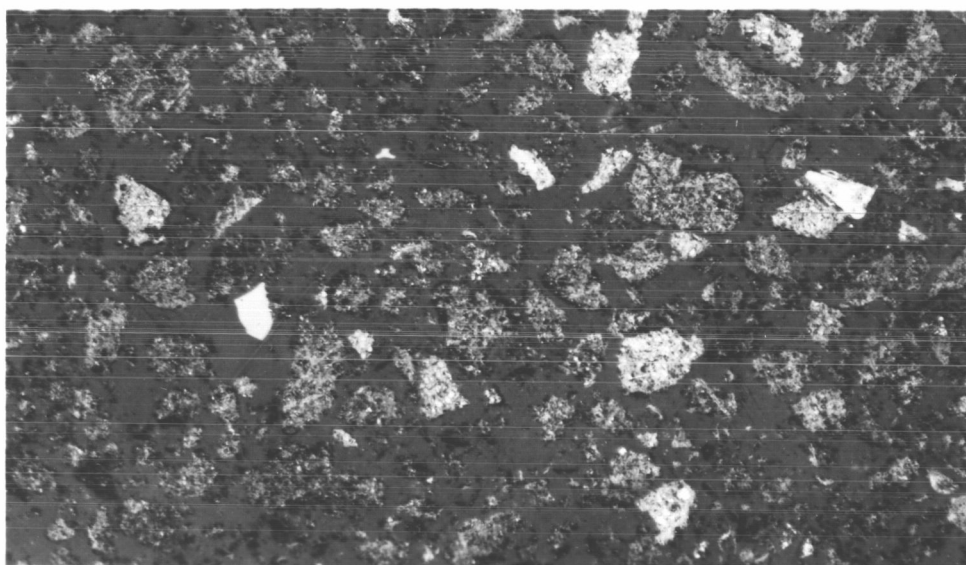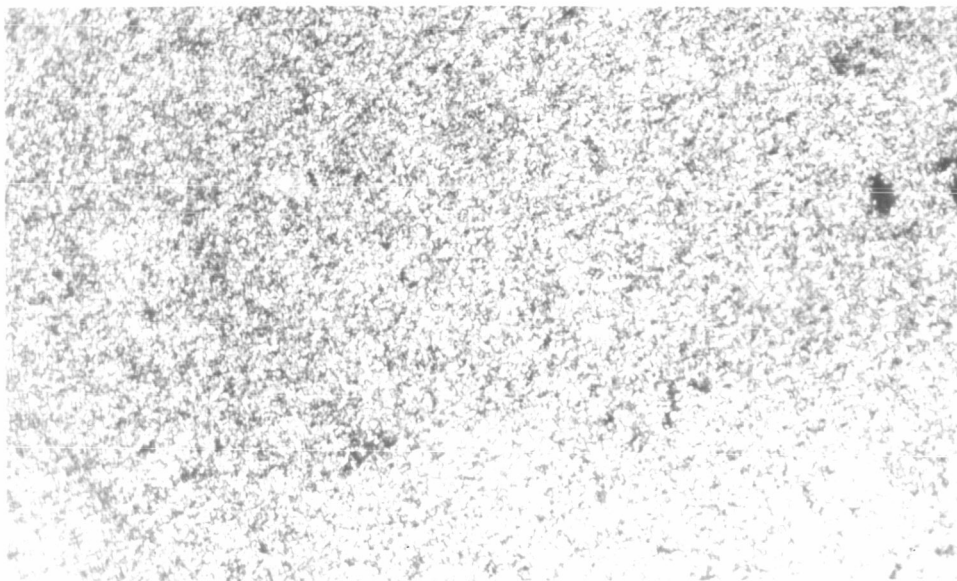
(a) High
    Expansion
    Graphite
    (Union
     Carbide)

Neg. 34054   Mag. X320
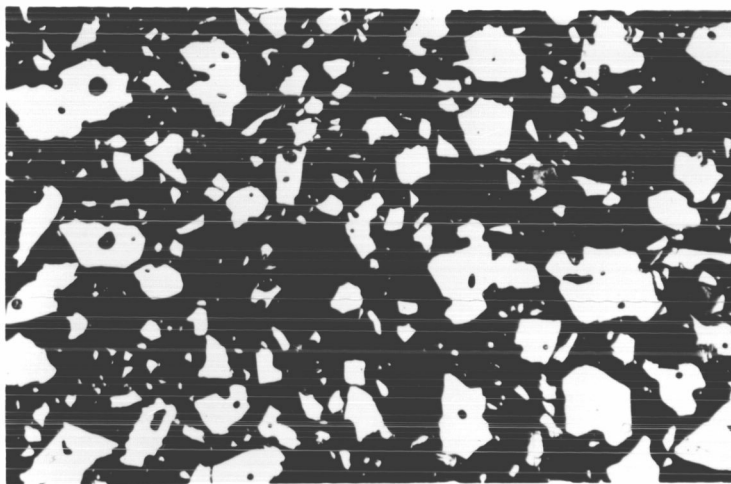

(b) Sterling
    10R
    (Carbon-
     black
     Cabot)

Neg. 34059   Mag. X1000

Fig. 1 - PARTICLE SIZE AND SHAPE OF CARBON POWDERS

50μ

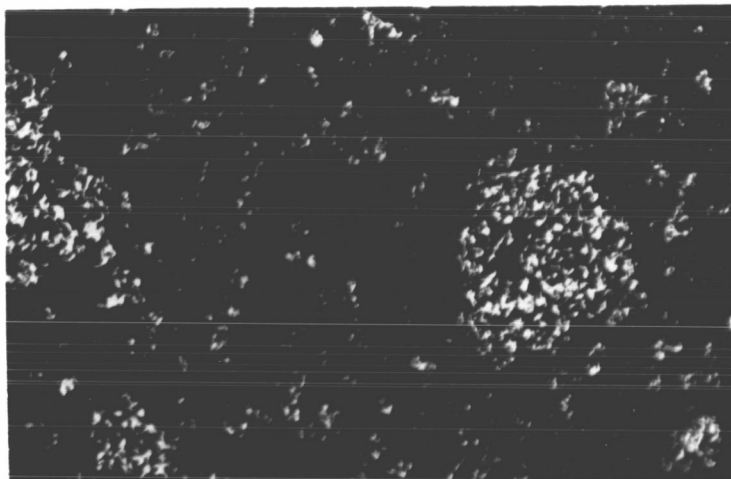(a) SP26713C
    (Wah Chang)

Neg. 34046   Mag. X320
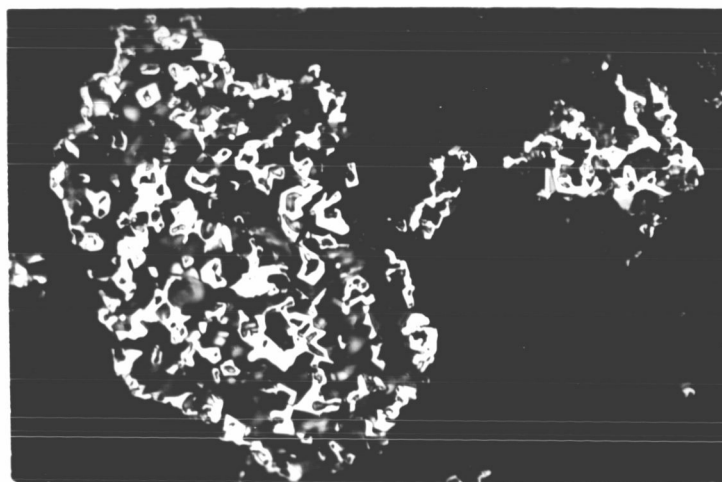
(b) Blend Nb-2
    (LASL)

Neg. 34048   Mag. X320

10μ

(c) Blend Nb-2
    (LASL)

Neg. 34060   Mag. X1000

Fig. 2 - PARTICLE SIZE AND SHAPE OF NbC POWDERS

B.   Processing

The mixtures of NbC and C were blended in the usual manner of tumbling for 16 hr with rubber stoppers. Mixtures were then loaded into the graphite dies for hot pressing. The Ceylon graphite mixture was extremely fluffy and required prior cold pressing at 10,000 psi in a steel die in order to yield a blend which would fit into the mold cavity.

The very fine particle size of Sterling 10R and the resulting high volume of material also necessitated special handling. The S10R-NbC blend was first immersed in methyl alcohol and then dried in order to obtain improved mixing without excessive aggregation. The mixture was then cold-pressed at 10,000 psi and hot pressed. However, operational problems forced a stoppage at 3000°C, so the billet (77.9% density) was crushed and the resulting powder blend was taken through the hot press cycle again. Thus, the Sterling 10R composite actually can be termed a "double pressing."

During hot pressing the time-temperature-pressure cycle was maintained a constant for the composites. The time required to attain the pressing temperature of 3150°C was approximately 1.5 hr. Each composite was soaked at this temperature for approximately 15 min under 3000 psi.

C.   Evaluation

1.   Compositional Designation

In order to facilitate simpler reference to the different compositions, the following abbreviations will be used in this report for the composites listed in Table I:

Table I

FABRICATION SUMMARY FOR NbC-C COMPOSITES HOT-PRESSED

USING DIFFERENT CARBON SOURCES

Compositional Designation	Starting Materials		Carbide Content		% Theoretical Density
	Carbon	NbC	Wt%	Vol%	
46.5NbC-1V	Varcum	30B	74.2	45.4	96.0
46.5NbC-1M2	M-2	30B	75.2	46.8	96.3
46.5NbC-1CPC	CPC	30B	74.0	45.2	97.4
46.5NbC-1Th	Thermax	SP26713C	75.1	46.6	95.8
46.5NbC-1Cy	Ceylon	SP26713C	75.3	46.8	94.6
46.5NbC-1G	Gilsonite	SP26713C	75.0	46.5	95.7
46.5NbC-1S10R	Sterling 10R	SP26713C	75.5	47.2	94.3
46.5NbC-2Hex	High Expansion Graphite	SP26713C	74.5	45.9	95.8
46.5NbC-3CPC	CPC	Blend Nb-2	74.8	46.3	96.8

| Designation	Abbreviation
46.5NbC-1V	V
46.5NbC-1M2	M2
46.5NbC-1CPC	1CPC
46.5NbC-1Th	Th
46.5NbC-1Cy	Cy
46.5NbC-1G	G
46.5NbC-1S10R	S10R
46.5NbC-2Hex	2Hex
46.5NbC-3CPC	3CPC

2. Fabrication

A fabrication summary for the various composites is tabulated in Table I. All composites were designed as 75 wt% or 46.5 vol% NbC compositions. As the metal analysis shows, little change in carbide content occurred for the various composites in processing. The extent of densification was similar for the billets, ranging from 94.3% for S10R to 97.4% for the CPC body. Although some variation in carbide content and % theoretical density was evident in any particular composite, the ranges were quite limited and the values presented in Table I can be considered representative.

3. Microstructure

The microstructure of the more recently fabricated composites, i.e., S10R, 2Hex, and 3CPC, are shown for both grain orientations in Figs. 3 through 5. Despite the gross difference in particle size between the Sterling 10R black (less than 0.1μ) and NbC (3.6μ), the resulting composite exhibits a fairly uniform dispersion of carbide in the graphite matrix (Fig. 3) with little porosity. In addition there is very little orientation of carbide grains from the pressing. This is in contrast to the other composites in which directionality for the carbide grains was evident to varying extents, even for the composite incorporating Thermax carbon black. It is possible that the very fine Sterling 10R carbon black may act almost like a fluid and give
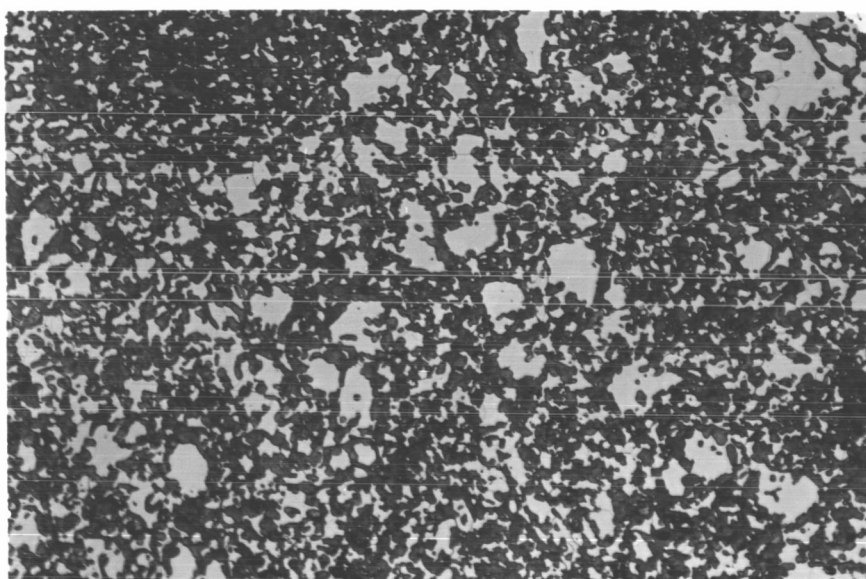
IIT RESEARCH INSTITUTE
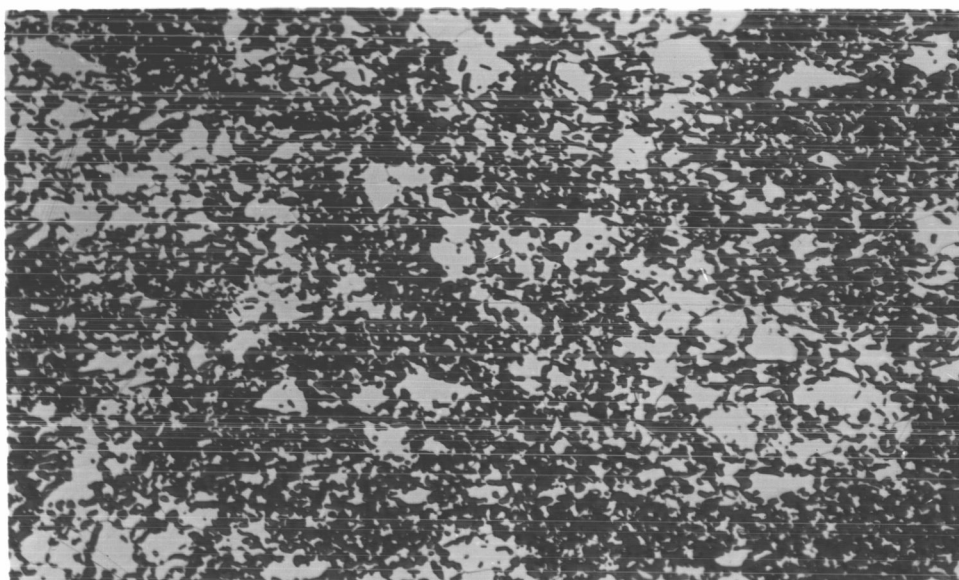
Neg. **34618**   **Mag.** X200

(a) Sample 6C-T
    (W/G)

Neg. **34617**   Mag. X200

(b) Sample 2B-L
    (A/G)

Etchant:
$K_3Fe_2(CN)_6$-NaOH

Fig. 3 - MICROSTRUCTURE OF NbC-C COMPOSITE
         INCORPORATING STERLING 10R CARBON BLACK

$\overline{|50\mu|}$
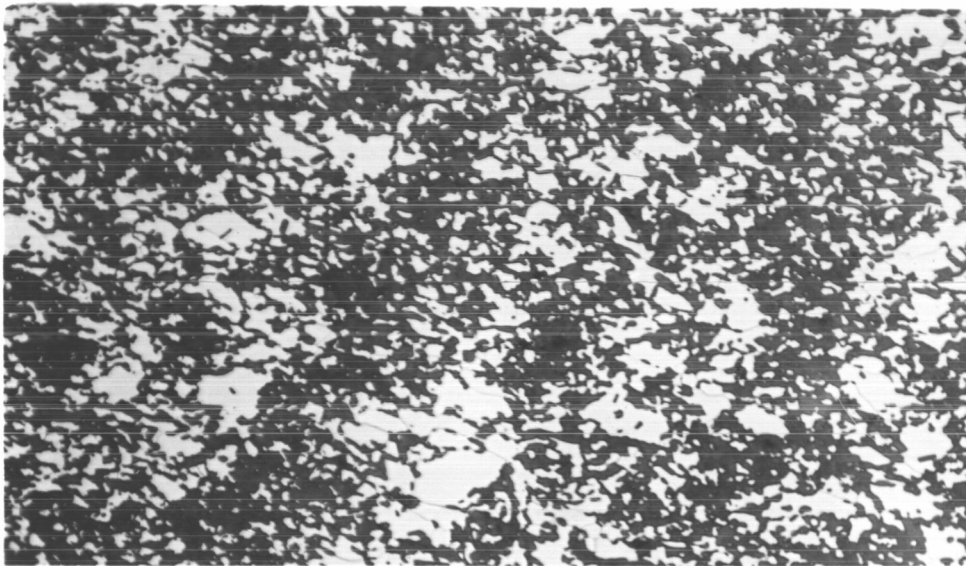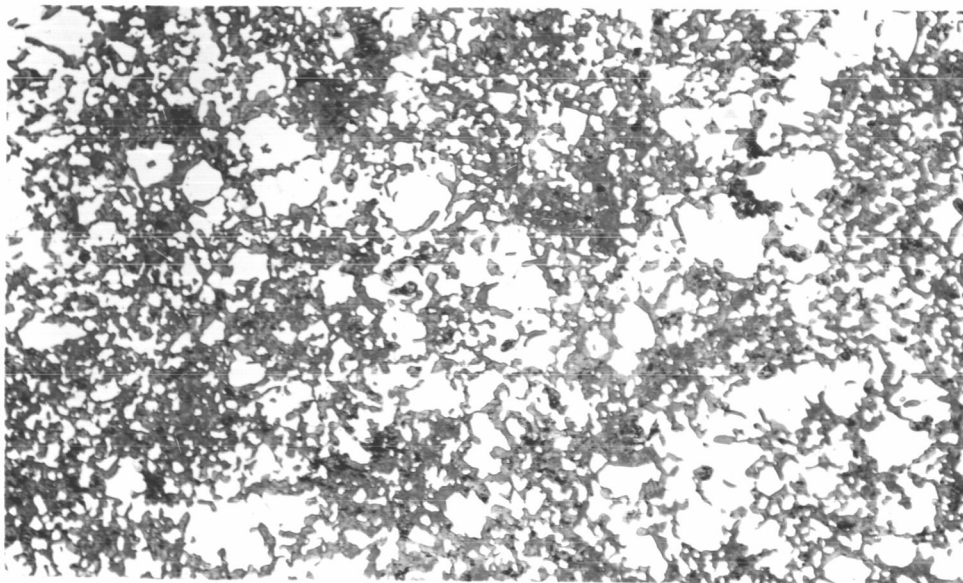

(a) Sample 3C-T
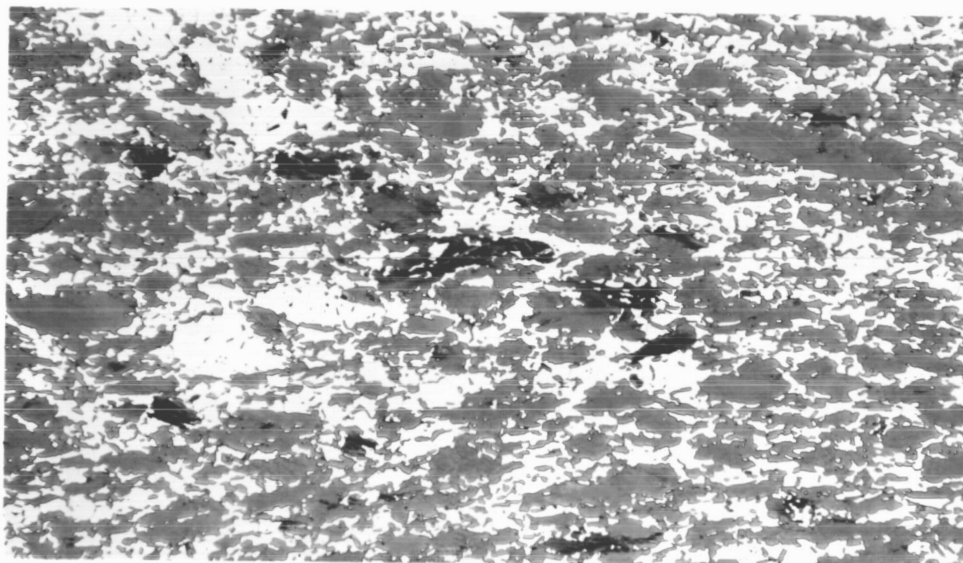   (W/G)

Neg. 34619   Mag. X200

(b) Sample 3B-L
    (A/G)

Etchant:
Neg. 34620   Mag. X200 $K_3Fe_2(CN)_6$-NaOH

Fig. 4 - MICROSTRUCTURE OF NbC-C COMPOSITE
          INCORPORATING HIGH EXPANSION GRAPHITE
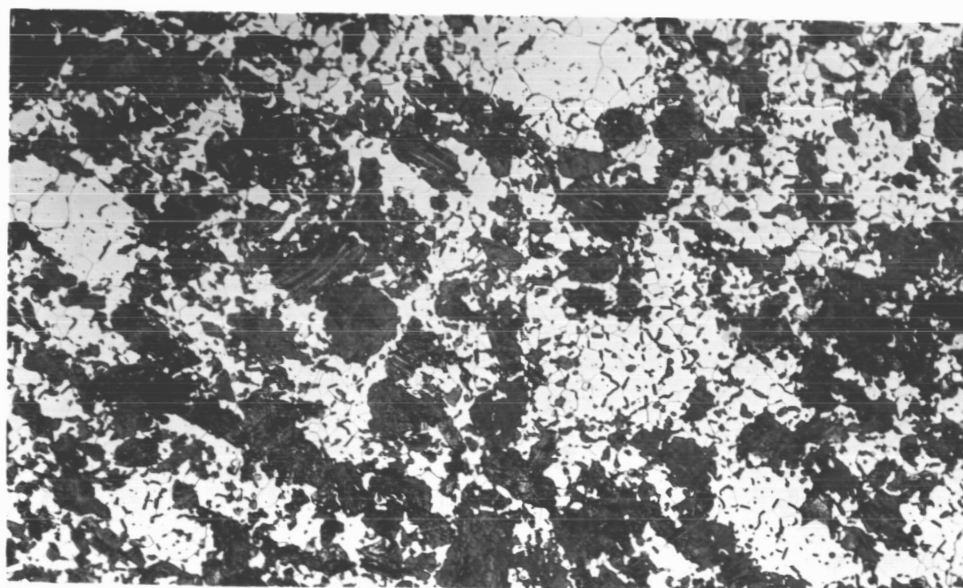
12

(a) Sample 3C-T
(W/G)

Neg. 34621   Mag. X200

(b) Sample 2A-L
(A/G)

Neg. 34622   Mag. X200

Etchant:
$K_3Fe_2(CN)_6$-NaOH

Fig. 5 - MICROSTRUCTURE OF NbC-C COMPOSITE
          INCORPORATING FINE NbC (BLEND Nb-2)
          AND CALCINED PETROLEUM COKE

rise to a limited isostatic condition in the biaxial hot-pressing.

The microstructure of 2Hex is similar in uniformity of dispersion although carbide grain orientation in the W/G direction is evident (Fig. 4). The 3CPC composite (Fig. 5) exhibits strong directionality, similar to that for Cy or 1CPC. Mixing was poor as evidenced by aggregation of the fine carbide. It may be necessary to pre-dry this very fine Blend Nb-2 or use special mixing methods to get good dispersion.

4.   Room Temperature Measurements:
       Flexural Strength and Moduli

As detailed in Table II, the W/G flexural strengths of the recently prepared composites (S10R, 2Hex, and 3CPC) were similar to those observed previously for the other 46.5 vol% NbC composites. The range which has been disclosed is about 14,000 to 19,000 psi. In the A/G direction, a very low strength of 4080 psi was exhibited by the 3CPC composite. As shown by its other properties, the 3CPC body was extremely anisotropic and topped the 1CPC body in directional behavior. This was somewhat surprising in that the use of a finer carbide was thought to be a method of realizing finer dispersion and less directionality. The strong directionality exhibited by the 3CPC composite may be due to a stronger orientation of the carbide phase. The finer carbide particles may be more sensitive to the load during hot pressing than a coarser carbide, resulting in pronounced alignment of carbide. This would minimize any bridging effect of carbide in the A/G direction.

The condition here differs from the isostatic effect suggested for Sterling 10R carbon black in that the carbide particles are forced into a horizontal distribution by the coarser

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Table II

PROPERTIES SUMMARY FOR NbC-C COMPOSITES HOT-PRESSED

USING DIFFERENT CARBON SOURCES

Compositional Designation	Grain Direction	Flexural Strength, psi			Elastic Modulus x10^{6}psi	Electrical Conductivity x10^{4}mho-cm^{-1}	C.T.E. x10^{-6}in/in/°C
		RT	2000°C	2500°C			
46.5NbC-1V	W/G	18,700	13,640	11,300	9.9	1.28	7.81
	A/G	10,580	9,270	7,070*	7.1	0.96	9.50
46.5NbC-1M2	W/G	16,860	18,810	14,900	8.7	1.24	8.28
	A/G	9,160	12,000	8,860	7.0	0.96	10.7
46.5NbC-1CPC	W/G	15,390	17,020	11,540	12.0	1.57	7.09
	A/G	7,380	11,690	6,530	5.1	0.89	11.1
46.5NbC-1Th	W/G	14,860	7,220	3,850*	8.4	1.01	6.66
	A/G	9,560	4,290	6,620*	5.8	0.73	13.0
46.5NbC-1Cy	W/G	16,620	11,760	8,880*	9.7	1.19	-
	A/G	5,070	3,740	3,530*	4.6	0.57	-
46.5NbC-1G	W/G	16,090	7,860	3,420*	10.3	1.13	-
	A/G	9,470	4,480	1,950*	6.0	0.74	-
46.5NbC-1S10R	W/G	13,510	17,760	10,800	8.6	1.00	8.03
	A/G	8,510	12,870	8,540	6.4	0.87	9.04
46.5NbC-2Hex	W/G	18,940	14,000	8,450*	8.8	1.38	7.02
	A/G	11,220	7,570	5,730*	6.3	0.83	10.5
46.5NbC-3CPC	W/G	14,330	18,000	11,710	12.1	1.56	-
	A/G	4,080	7,680	6,580	3.9	0.72	-

* Highest stresses which could be applied prior to rapid deformation. Other samples were stressed to failure.

needle shape of the CPC. In the case of the spherical S10R, there would not be a tendency for such alignment to occur; furthermore, the coarser carbide phase is irregular in particle shape and not as susceptible to strong alignment.

The flexural moduli values (Table II) were also quite similar (8.4 to 12.0 x 10^6 psi) to those observed for the other composites (8.6 to 12.1 x 10^6 psi). The 3CPC composite again exhibited high anisotropy; the W/G value was quite similar to that for 1CPC (12.1 vs 12.0 x 10^6 psi) but the A/G value was significantly lower (3.9 vs 5.1 x 10^6 psi).

Anisotropy - Anisotropy ratios appear in Fig. 6. The highest ratios exist for the composites incorporating the needle coke (1CPC and 3CPC) and Ceylon graphite (Cy). This behavior reflects the highly directional particle shapes of these carbons. Microstructural studies have shown that the carbide particles also show a strong tendency to align perpendicular to the pressing direction.

Lowest anisotropy was exhibited by the V, M2 and S10R composites. The more isotropic behavior of these composites can be considered even more desirable in that the W/G strengths are about equivalent to those for the CPC and Cy composites, while the A/G strengths are significantly higher. Thus, the trend toward isotropy is gained without sacrifice in strength. Furthermore, the moduli values for V, M2 and S10R (9.9, 8.7, and 8.6 x 10^6 psi) are lower than those for 1CPC, 3CPC and Cy (12.0, 12.1 and 9.7 x 10^6 psi). This is desirable in thermal shock considerations.[1]

Electrical Conductivity - Electrical conductivity data are tabulated in Table II, and conductivity-strength relationships are shown graphically in Fig. 7. The data for S10R and 2Hex
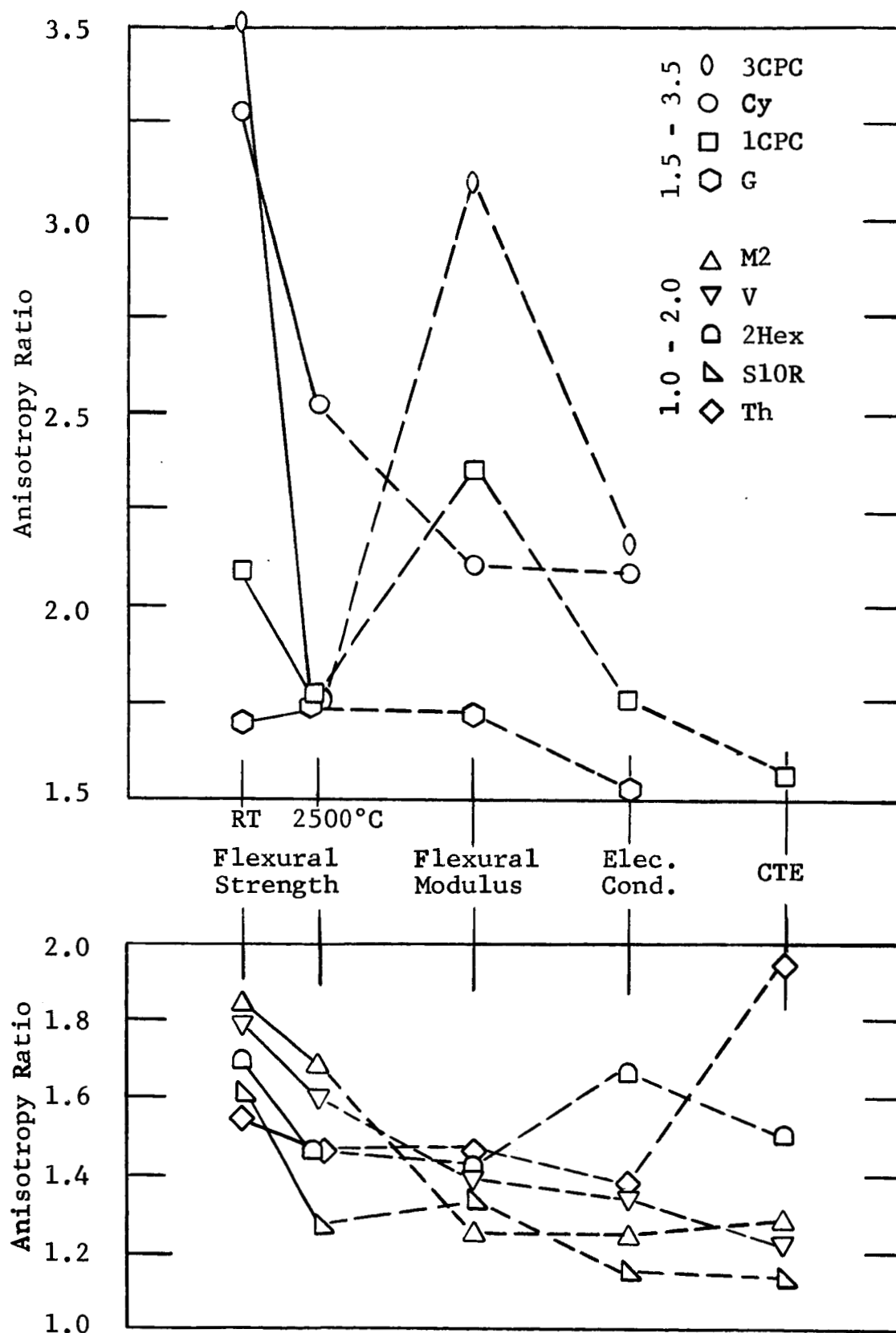
Fig. 6 - ANISOTROPY IN PROPERTIES FOR NbC-C COMPOSITES
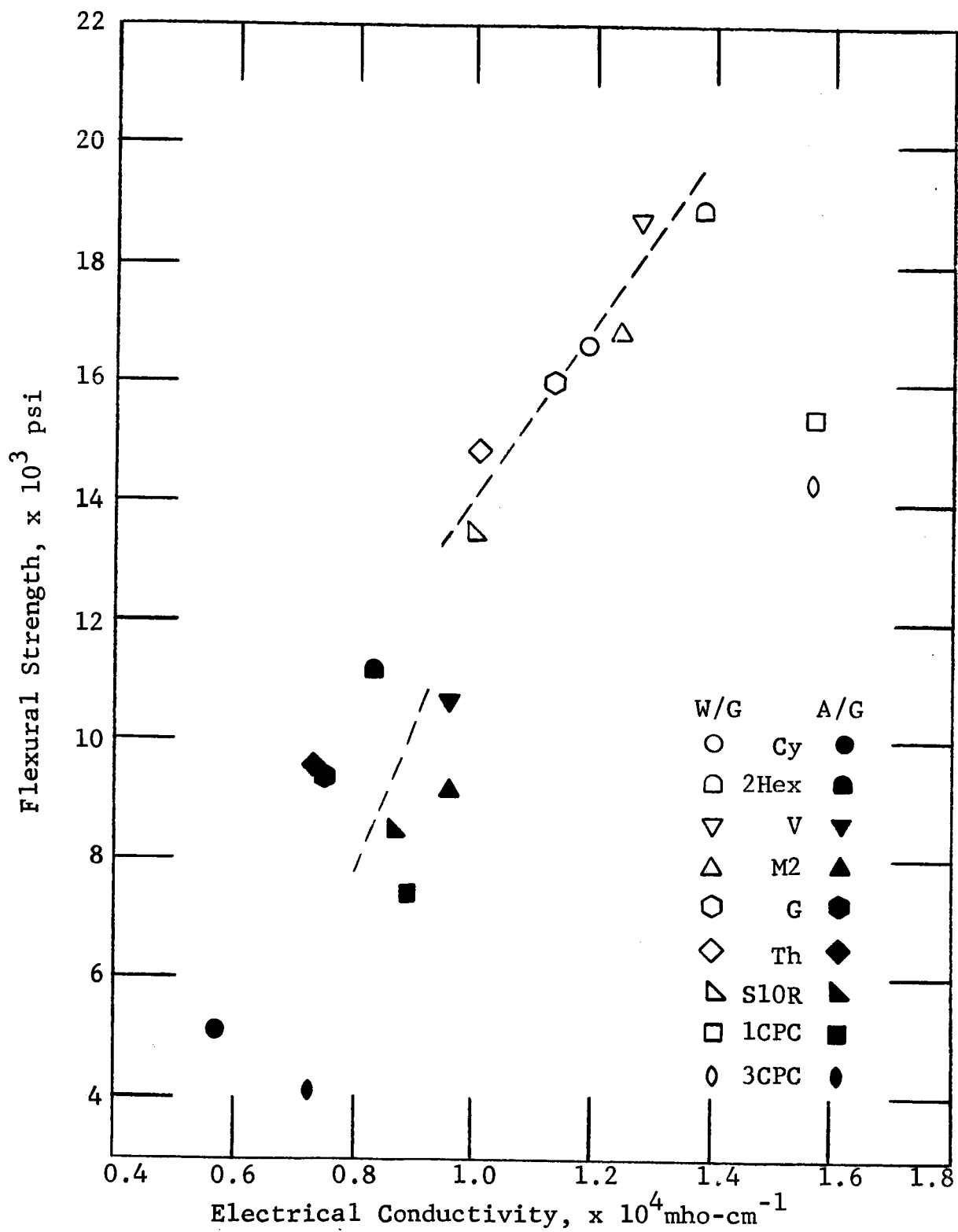FABRICATED USING DIFFERENT CARBON SOURCES

Fig. 7 - ELECTRICAL CONDUCTIVITY VS FLEXURAL STRENGTH
FOR NbC-C COMPOSITES FABRICATED USING DIFFERENT
CARBON SOURCES

appear to fit the linearity previously pointed out for the Cy, V, M2, G, and Th composites. The 3CPC, on the other hand, is much more conductive and is paired with 1CPC. Apparently the graphite phase in CPC composites is much more conductive than that formed in composites using other carbon sources. This may be due to a higher degree of ordering of the graphite phase, although it would seem that the composite incorporating natural graphite (Cy) should be equally well ordered. X-ray and further metallographic studies will be conducted to determine if this is indeed the factor.

Another condition for higher electrical conductivity could be continuity in the carbide phase; the resistivity of NbC is an order of magnitude lower than that of graphite. However, microstructural studies have shown that such a skeletal network might exist in the V or M2 composite but not in the CPC bodies. As the data in Table II and Fig. 7 show, the electrical conductivity for V and M2 are about $1.25 \times 10^4 \text{mho-cm}^{-1}$ as compared to $1.56 \times 10^4 \text{mho-cm}^{-1}$ for 1CPC and 3CPC.

Electrical measurements continue to be a good indication of bonding within any single system. Where variations in strength have existed in a billet, conductivity measurements have been a highly sensitive reflection of such differences. On the other hand, density data have been quite insensitive to such variations.

5.   High Temperature Measurements:
      Flexural Strength

Differences in behavior of the various composites fabricated using different carbon sources were quite pronounced in high temperature tests. Flexural strengths at 2000° and 2500°C are tabulated in Table II and illustrated in Figs. 8 and 9.
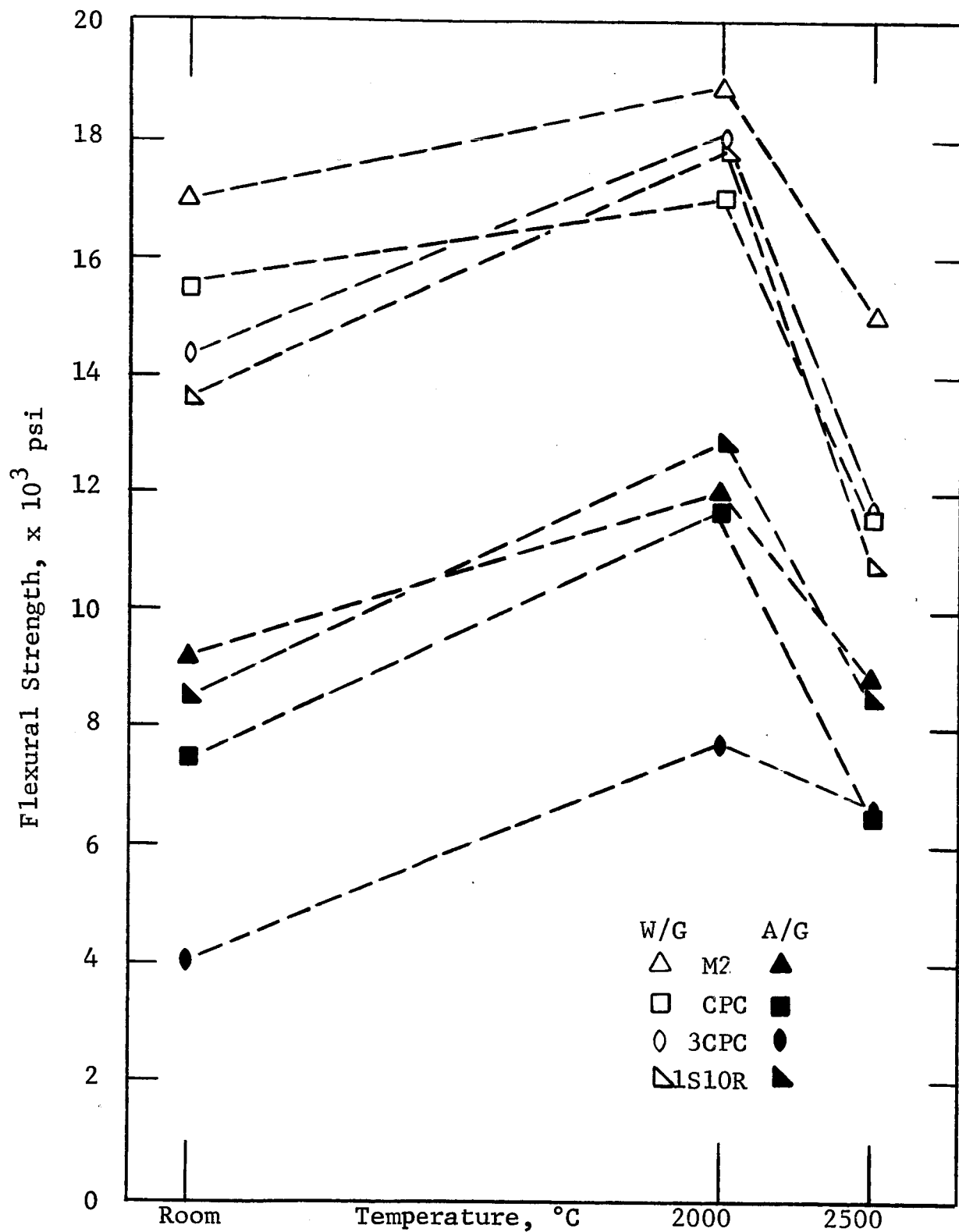
Fig. 8 – FLEXURAL STRENGTH VS TEMPERATURE
FOR NbC-C COMPOSITES FABRICATED USING
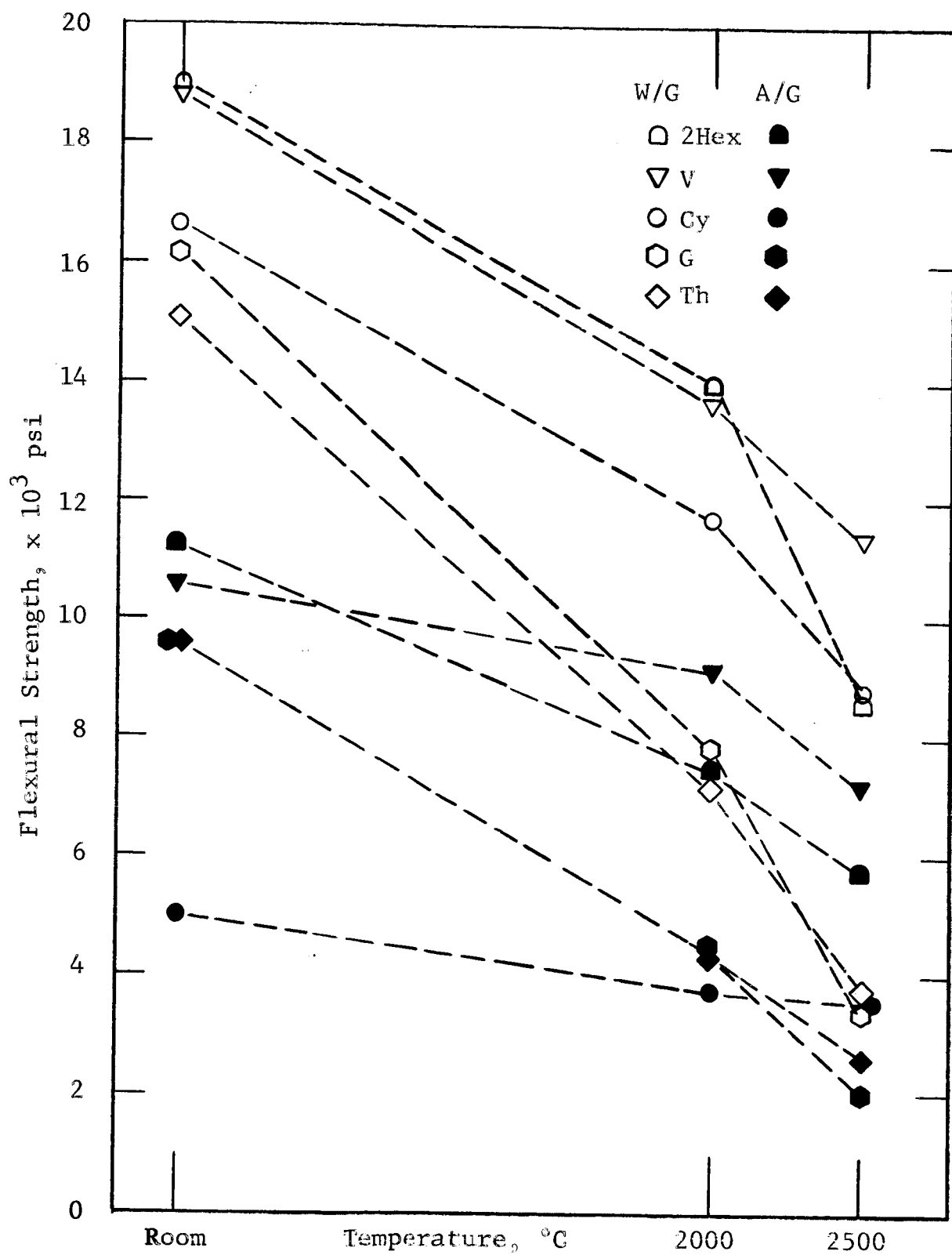DIFFERENT CARBON SOURCES (Series I)

Fig. 9 — FLEXURAL STRENGTH VS TEMPERATURE FOR NbC-C COMPOSITES FABRICATED USING DIFFERENT CARBON SOURCES (Series II)

The nine composites have been separated into two groups: Series I (Fig. 8) include those which exhibited an increase in strength at 2000°C, and Series II (Fig. 9) are those which showed a decrease in strength with temperature.

The composites which had higher strengths at 2000°C were M2, 1CPC, 3CPC and S10R. As shown in Fig. 8, there was a drop-off in strength at 2500°C. This behavior is similar to that observed for CPC-containing composites in earlier studies.[1] The other composites all showed decreased strengths at the elevated temperatures. In the 2500°C tests, all samples (with the exception of V-W/G) could not be stressed to failure. The stress levels shown are the highest which these samples could sustain; continuation of tests resulted in rapid plastic deformation and subsequent "bottoming" of samples on the test boat.

Some of the possible reasons for the decrease rather than an increase in strength are summarized in the following sections.

a.   Composites Containing Carbon Instead of Graphite

The decrease in strength with temperature is characteristic of carbon. For the Series II materials, the V, G and Th composites may still contain appreciable carbon, but it is unlikely that such a condition could exist for Cy or 2Hex which both used graphites as raw materials. Furthermore, S10R which showed an increase in strength with temperature can be classed as one of the most difficult to graphitize. Thus, this may be the reason for poor high temperature behavior for some (V, G, and Th) of the composites, but it would not be applicable for Cy or 2Hex.

b.   Impurities Giving Rise to Plastic Deformation

Other investigators have reported that impurities, particularly iron, have an adverse effect on resistance to high

temperature deformation.[6] The susceptibility to creep would be relfected in lower apparent strength. This may be the reason for the poor high temperature behavior of 2Hex since the high expansion graphite was prepared from coke incorporating 2% iron oxide.

c.   Degree of Bonding

It is possible that carbide-graphite bonding may be weakened at higher temperatures by thermal expansion differences. With poorer bonding, creep by grain boundary slip is quite possible.

In addition to the factors described above, conditions such as porosity and size and shape of pores would also influence strength and creep. To analyze the effect of impurities, our raw carbons are now being characterized for their morphology as well as purity by LASL. As soon as this information is available, attempts will be made to correlate high temperature behavior with impurity level.

As pointed out in the Electrical Conductivity Section, x-ray and metallographic studies are being conducted to determine extent of graphitization and its role in composite properties. This may provide some insight into the above mentioned differences in behavior of the various composites.

The trend toward isotropic behavior at higher temperatures has been noted in previous reports.[1] Anisotropy ratios for flexural strength data at 2500°C plotted in Fig. 6 reveal this trend for the various composites. This behavior results from a more rapid decline in W/G strength as compared to A/G strength at 2500°C. For example, the data on Fig. 8 show that the 2500°C strengths as compared to room temperature strengths are considerably lower in the W/G direction whereas for the A/G direction, it is about the same. It is possible that this is

due to greater stresses in the A/G direction arising from the hot pressing, such that the room temperature A/G values are "abnormally" low. These stresses, of course, would be relieved in the higher temperature tests.

Coefficient of Thermal Expansion - CTE values for several of the composites are tabulated in Table II and represented in Fig. 10. Also plotted in Fig. 10 are anisotropy ratios of A/G to W/G values. In general, the data follows the directional relationships observed in other properties, e.g., 1CPC which was one of the more anisotropic composites in terms of strength exhibited a fairly high CTE ratio. One exception was the Th composite which was observed to be very anisotropic. This departure from its more isotropic behavior in other properties is shown in Fig. 6. Such strong directional expansion differences are usual for highly oriented graphite, a condition which the Th composite does not satisfy. Additional tests will be conducted to investigate this strange behavior.

The S10R was the most isotropic in behavior. This concurs with its other properties as depicted in Fig. 6. The absolute values of 8.03 (W/G) and 9.04 (A/G) x 10^{-6} in./in./°C are quite close to the value for pure NbC[7] of 8.50 x 10^{-6} in./in./°C in the range room temperature to 2500°C.

Flexural Creep - An important consideration in the utility of a structural material at high temperatures is its resistance to plastic deformation. In order to determine high temperature structural integrity, the various materials were subjected to flexural creep tests (four-point loading) at 2000° and 2500°C. The stress level was set at a fairly high 5000 psi in order to exaggerate differences among the composites.
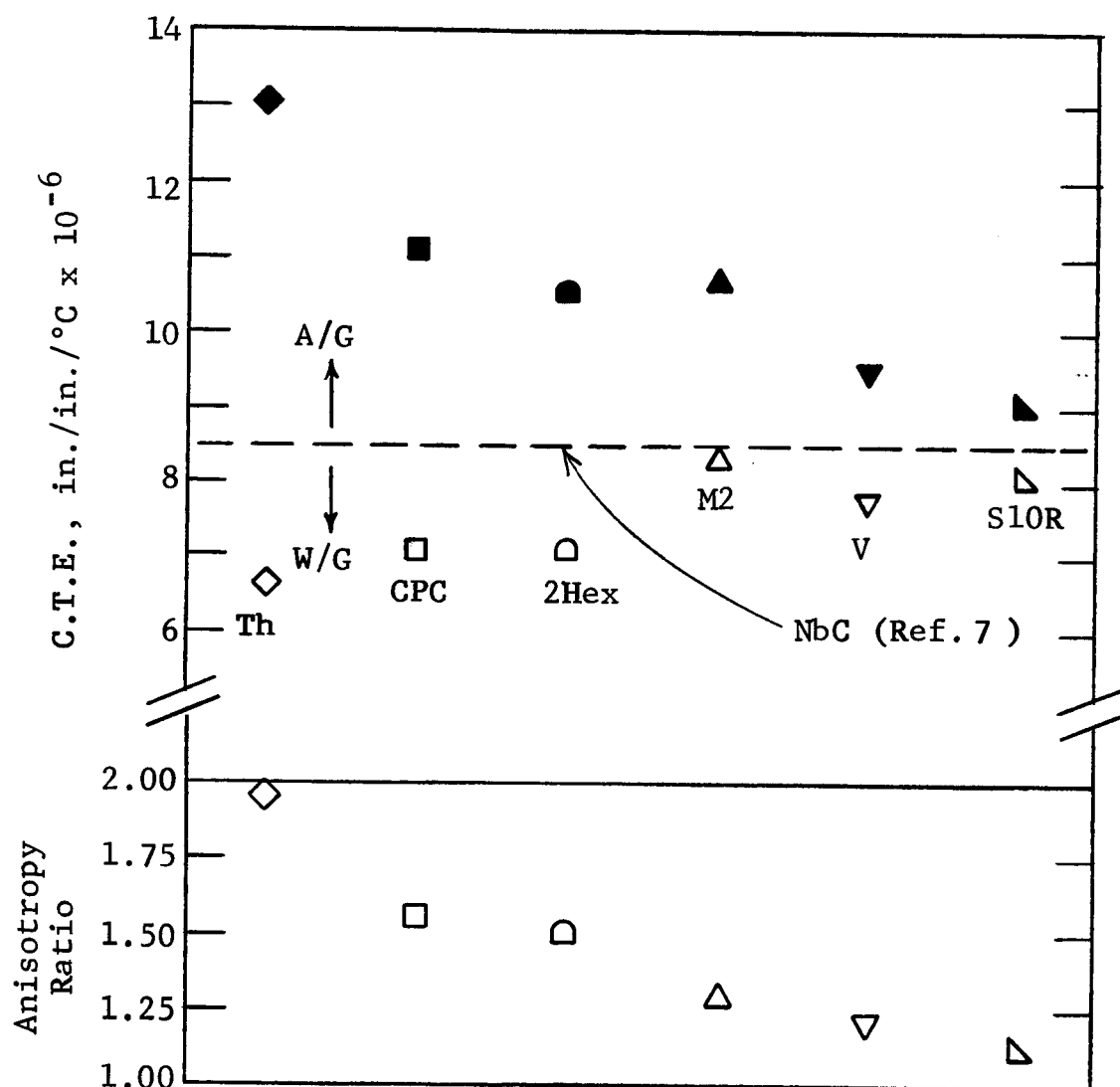
Fig. 10 - COEFFICIENT OF THERMAL EXPANSION
FOR NbC-C COMPOSITES FABRICATED
USING DIFFERENT CARBON SOURCES
(Room Temperature-2550 °C)

The total deflection observed for these various materials are depicted in Fig. 11, and the creep rates are shown graphically in Figs. 12 (2000°C) and 13 (2500°C). Under the conditions 2000°C/5000 psi/30 min, the order of resistance to creep in the W/G direction was: S10R, CPC, M2, 3CPC and V. In the A/G direction the smallest deflection was shown by M2 with slightly higher deformations for S10R, CPC, V, and 3CPC. The other samples, i.e., Th, G, Cy and 2Hex showed relatively high deformation. In the A/G direction the stress level of 5000 psi was too high for Th, G and Cy, so a load equivalent to 3000 psi was used. Even under these reduced loads, these composites exhibited very large and high rates of deformation in the A/G direction and the experiments were terminated after a deflection of 2mm.

Deformation, of course, was considerably exaggerated in the 2500°C studies. As the graph in Fig. 11 shows, CPC and V exhibited the best creep resistance in the W/G measurements. At this level, M2 displayed fairly strong deformation which was significantly higher than that shown by CPC or V. In the A/G direction, very rapid deformation occurred; two of the tests (V and CPC) were terminated before the 30 min duration due to "bottoming" of the test specimen on the bottom boat. Apparently the stress level in A/G tests must be reduced, perhaps to 2000 or 3000 spi, in order to gain meaningful differences between the composites.

Although the data is not shown on the graphs, very recent tests with S10R has revealed that this material shows the best resistance to creep. In the W/G direction, deformation was .69mm which is slightly less than that for V (.74mm) or CPC (.79mm). It is in the A/G direction that S10R shows a clear superiority to the other materials tested. The deflections were:
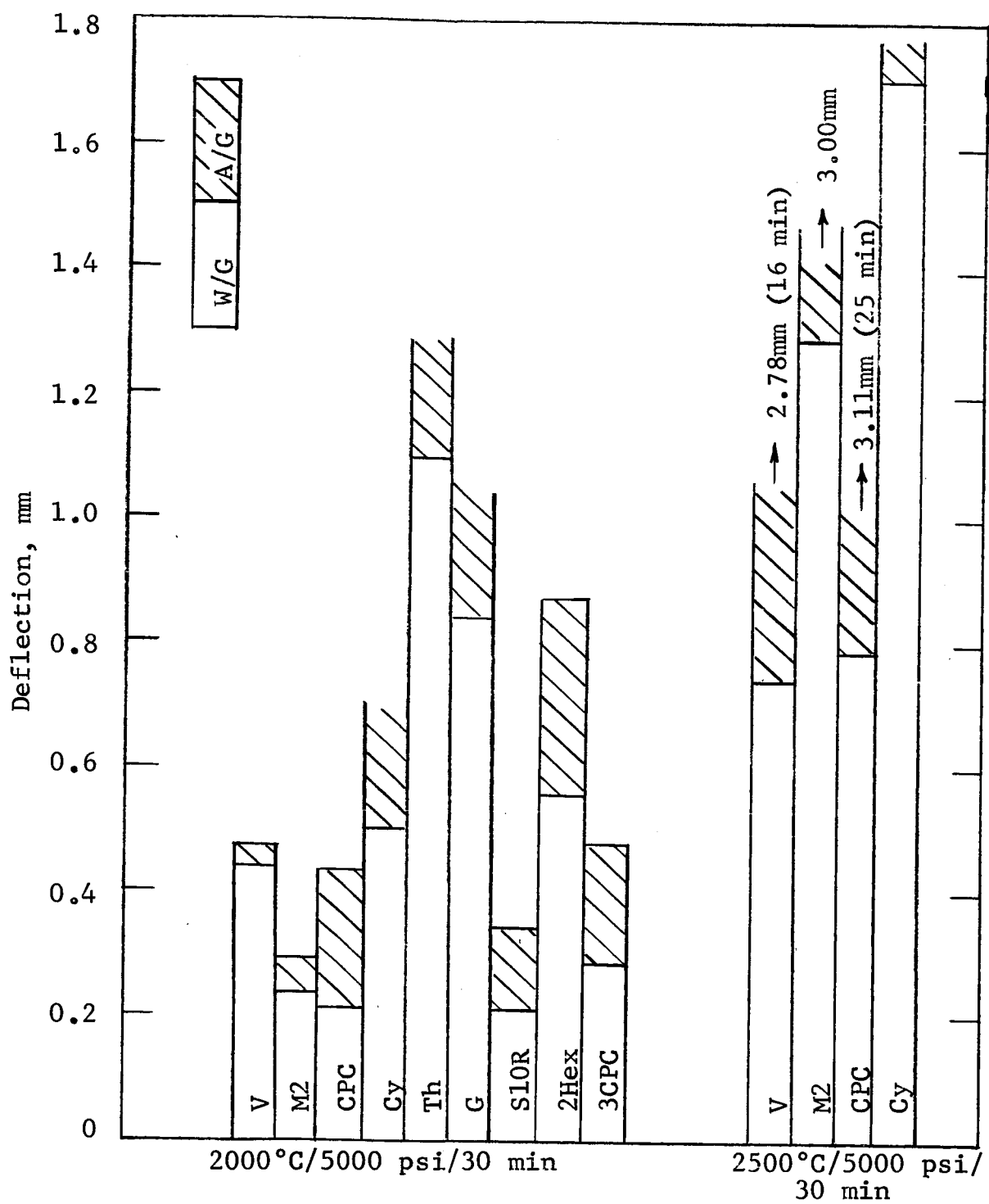
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Fig. 11 – FLEXURAL CREEP FOR NbC-C COMPOSITES FABRICATED
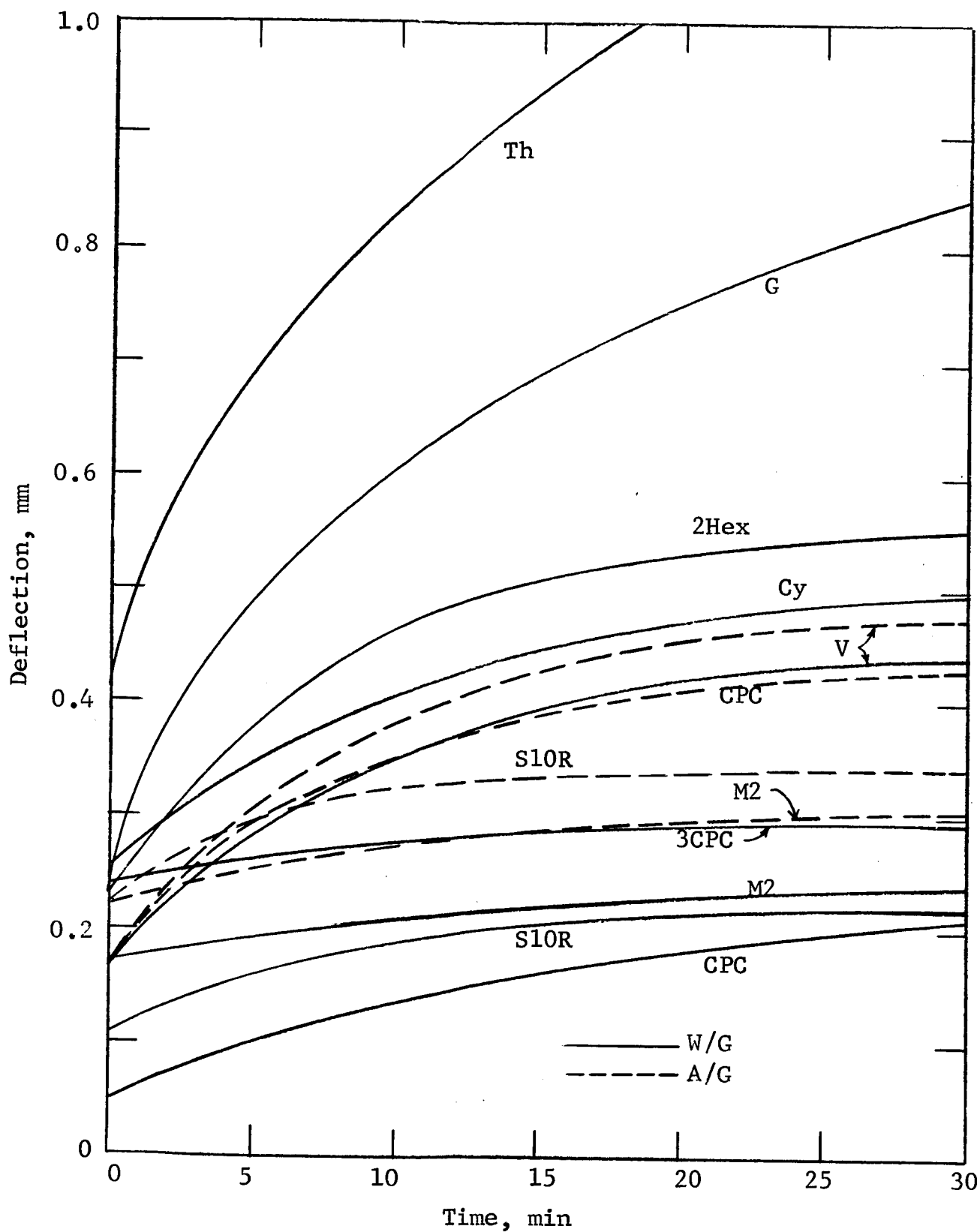USING DIFFERENT CARBON SOURCES

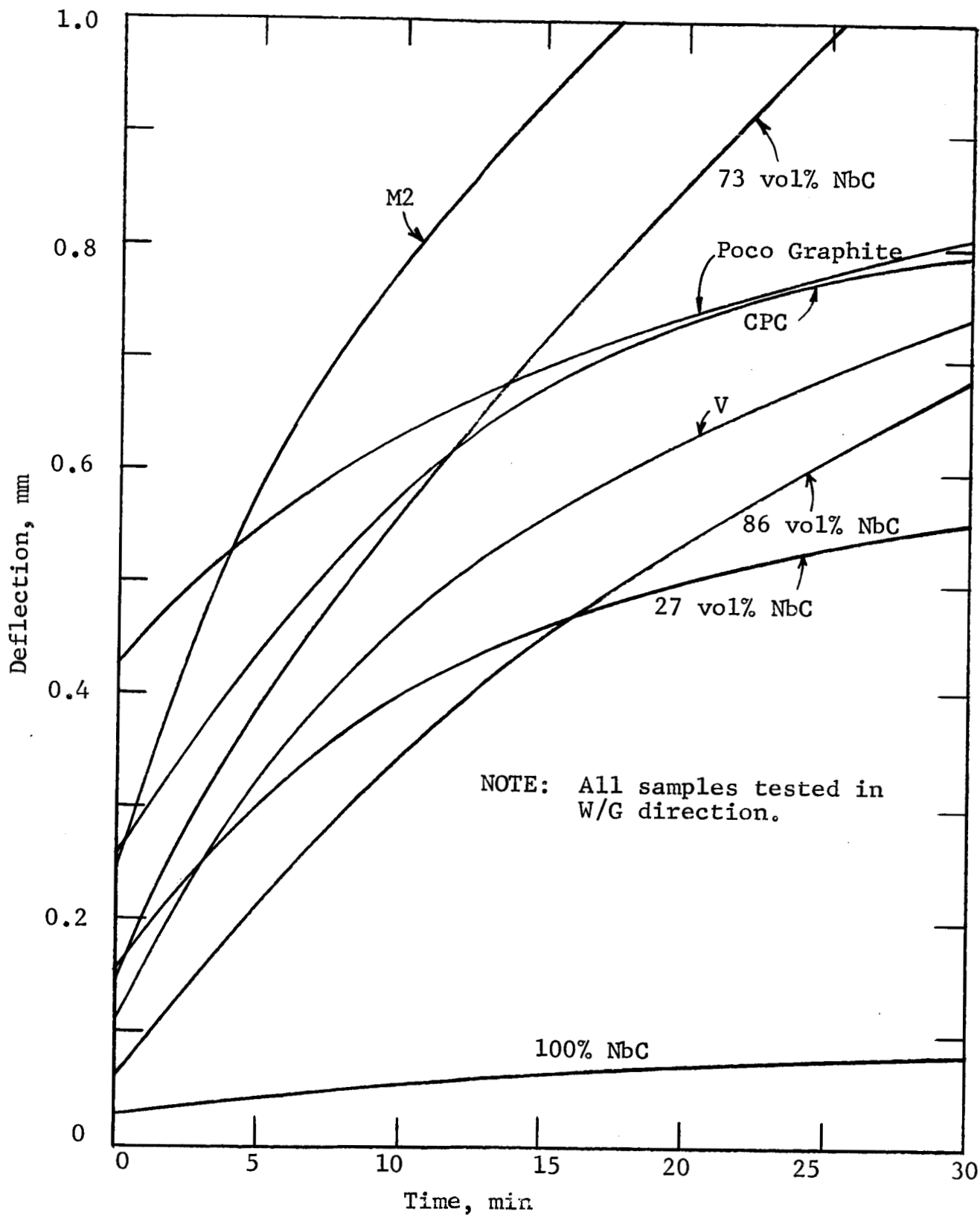Fig. 12 - FLEXURAL CREEP OF NbC-C COMPOSITES
(2000°C, 5000 psi, 30 min)

Fig. 13 - FLEXURAL CREEP OF NbC-C COMPOSITES,
POCO GRAPHITE, AND PURE NbC
(2500°C, 5000 psi, 30 min)

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S10R    - 1.11mm
M2      - 3.00mm
V       - 3.18mm (extrapolated)
CPC     - 3.72mm (extrapolated)
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It has been reported that creep in a graphite will be
smaller as the degree of graphitization increases and as the
grain size within the material is smaller.[8] The latter condition
of smaller grain size is probably satisfied by the S10R. The
excellent A/G behavior of S10R may be attributed to a rather
random particle orientation as revealed in microstructural
studies. There was no indication of strong grain alignment per-
pendicular to the pressing direction such as that seen for CPC
or Cy, and this isotropic nature was observed in the other prop-
erties for S10R. The first condition, i.e., increased degree
of graphitization leading to improved creep resistance, appears
to be violated by the behavior of Cy. As has been reported,
impurities can be a significant effect on creep behavior, and
this may be the reason for the relatively high creep seen for
Cy. The factors which can influence creep are several in number,
e.g., porosity itself can be a factor in terms of amount, size
and shape. The complexities involved in creep behavior demand
careful analysis of several factors in order to determine the
properties of NbC-C composites which we must control to obtain
good creep resistance. Additional information is now being
gathered in an attempt to make these analyses.

Our studies are further complicated by the fact that
we have a two-phase composite. At this carbide level of 46.5 vol%,
the graphite phase appears to be a strong influence on properties.
Pure NbC exhibits very low creep at 2500°C; the higher deforma-
tions observed for the NbC-C composites as well as the variations
among the composites indicate that the influence of NbC is limited.
Furthermore, the dominance of graphite can be observed by com-
paring 1CPC (coarse NbC) and 3CPC (fine NbC). The various

properties including flexural creep were quite similar, suggesting that the use of a finer carbide to obtain a finer dispersion has little effect. The influence of particle size variations for a single carbon source will be one of the studies to be conducted in the near future.

Flexural Creep vs Carbide Content - Tests were also conducted at 2500°C with NbC-C composites incorporating CPC and of varying carbide contents. The results of these studies are shown in Fig. 13 (creep rate) and Fig. 14 (creep vs carbide content). In Fig. 14, deflections after the initial loading to 5000 psi, after the 30 min under load, and after removal of load, are shown. A peak exists at the 47 vol% NbC for Δ after initial load, showing that this composition may be considered as having the lowest modulus at 2500°C. Deformation after the 30 min duration of the test was greatest for the 72 vol% NbC composite. A similar peak was seen to exist in compressive deformation studies, both at IITRI[1] and LASL.[9]

Pure NbC displayed remarkably good resistance to creep. This was somewhat unexpected in view of earlier experiments in which NbC had shown greater deflection than NbC-C composites incorporating 17, 52 or 86 vol% NbC. However, the stress level in the previous studies was 10,000 psi whereas the present studies are at 5000 psi. Examination of the stress-deflection curve for NbC up to 10,000 psi shows that the deformation becomes quite rapid above 6000 psi. It would appear then, that 5000 psi is lower than the stress necessary (critical resolved shear stress) for appreciable deformation in pure NbC.

Another significant finding was the A/G behavior of these composites of varying carbide content. As Fig. 14 shows, creep in the A/G direction for the high carbide content (86 vol% NbC) was virtually the same as in the W/G direction. This
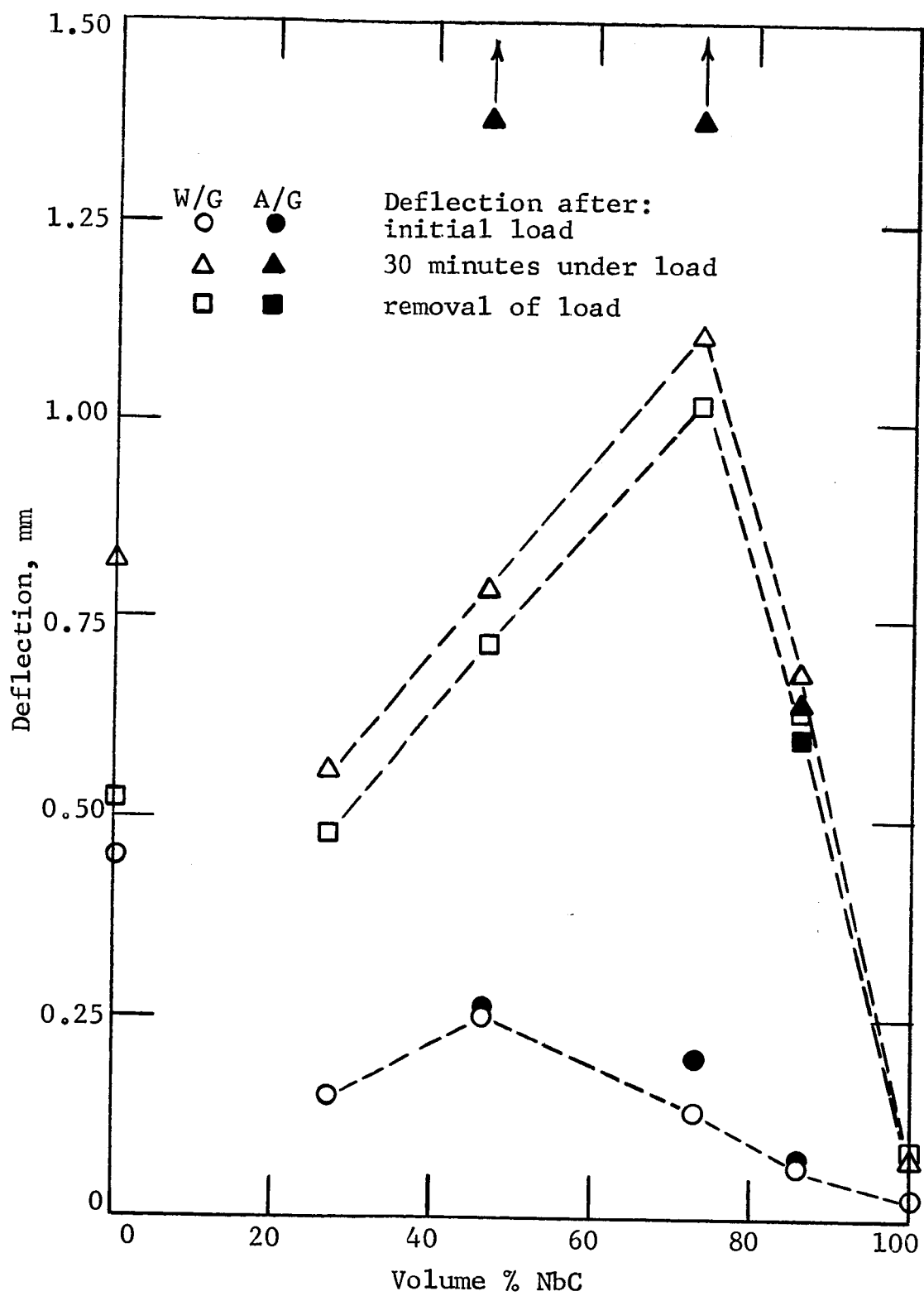
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Fig. 14 - FLEXURAL CREEP VS CARBIDE CONTENT
FOR NbC-C COMPOSITES
(2500°C, 5000 psi, 30 min)

correlates with the trend toward isotropy with increasing carbide content discussed in our Summary Report.[1]

III. CONCLUSIONS AND FUTURE WORK

Examination of the high temperature behavior of NbC-C composites fabricated using different carbon sources has revealed significant differences not indicated in room temperature studies. These studies have shown that properties are greatly influenced by choice of materials. For example, strongly anisotropic behavior is realized using a needle coke such as CPC; isotropic behavior is obtained through the use of spherical particles of S10R. Data has been obtained which will aid in determining causes of high temperature deformation; these studies should reveal directions for optimum high temperature properties. The outstanding creep resistance shown by certain composites suggest narrowing of our carbon cources to a selected few. The following findings are considered the most significant for this period:

1. At a carbide content of 46.5 vol%, composites incorporating Sterling 10R (S10R) carbon black show the best high temperature behavior. Its resistance to flexural deformation, particularly in the A/G direction was superior to that for any of the composites tested. The S10R composite also exhibits low anisotropy in its properties. Of particular significance, perhaps, is the thermal expansion behavior for which the A/G to W/G ratio is 1.13.

2. The composites incorporating Varcum (resin coke), M-2 (synthetic graphite) and CPC (calcined petroleum coke) also displayed good high temperature properties. Studies of these materials will take a secondary role to examination of S10R.

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Future work will consider closer examination of the various composites by techniques such as x-ray, metallography, and microprobe analysis in attempts to determine factors leading to different high temperature behavior. One experiment will involve deliberate doping of an NbC-C composite with amounts of iron up to 1% to determine the role of impurities.

In other studies the effect of variations in particle size relationships between the graphite phase (single carbon source) and NbC (particle size = constant) will be analyzed. In addition, the use of densification aids in the TaC-C system will receive study. In view of its outstanding behavior, S10R studies will be escalated.
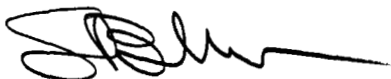
IV. CONTRIBUTING PERSONNEL AND LOGBOOK RECORDS

The following personnel have been involved in this research program: S. A. Borta, Y. Harada, J. L. Sievert and C. J. Levesque. Data are detailed in Logbook Nos. C 18063, C 18070, C 18080, C 18233, C 18267, and C 18363.

Respectfully submitted,
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